

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of : March 3, 2003
Deitz et al. : Group Art Unit: 1754
Serial No. 09/833,603 : Examiner: C. A. Ildebrando
Filed: April 13, 2001 : Docket No.: W-9515-01
For: Zeolite Based Catalyst of Ultra-High
Kinetic Conversion Activity

DECLARATION UNDER 37 CFR 1.132

Assistant Commissioner of Patents
Washington, D.C. 20231

Dear Sir:

I, Wu-Cheng Cheng, declare and state as follows:

1. I am a citizen of the United States of America and presently reside at 10308 Paddington Court, Ellicott City, Maryland 21042.

CERTIFICATE OF MAILING UNDER 37 C.F.R. §1.8

Pursuant to 37 CFR §1.8, I hereby certify that I have a reasonable basis to expect that this correspondence will be deposited with the United States Postal Service on or before the date indicated, as First Class mail, in an envelope addressed to: Director of Patents and Trademarks, Washington, D.C. 20231.

Date

Signature

2. I received by undergraduate education at the Massachusetts Institute of Technology and received a B.Ch.E. from the Institute in June of 1979. I, further, conducted graduate studies in Chemical Engineering at Leland Stanford Jr. University and received a Ph.D. degree from the University in June of 1984.

3. From 1983 to the present I have been employed by W.R. Grace & Co.'s Davison Division and presently hold the title of Research and Development Fellow. A substantial portion of my research and development activities has been directed to the synthesis and evaluation of fluid cracking catalysts and processes using same.

4. I am one of the named applicants of the above-identified patent application and am fully aware of the technology to which it is directed.

5. I have read and understand the contents of the Official Action issued September 5, 2002 with respect to the Application for U.S. Letters Patent having Serial No. 09/833,603, filed April 13, 2001.

6. I have read and understand the content of each of the following references, which have been used as the basis for rejections in the above-identified Official Action:

U.S. Patent 6,022,471 to Wachter et al.
U.S. Patent 5,120,693 to Connelly et al.
U.S. Patent 5,079,202 to Kumar et al.
U.S. Patent 5,055,437 to Herbst et al.
U.S. Patent 4,918,036 to Rheaume et al.
U.S. Patent 4,442,223 to Chester et al.

7. The following experiments were carried out by me or by others under my supervision, direction and control and are presented hereunder to compare the presently claimed catalyst composition to catalyst compositions

disclosed and taught in the cited reference of Wachter et al. The showings made hereunder clearly establish that fluid cracking catalysts composed of very high content of a high activity zeolite in an alumina sol matrix according to the present invention unexpectedly have the combined properties of high kinetic activity, high bulk density and low attrition properties, as well as high surface area and pore volume, which combination is highly desired for fluid cracking applications. In contrast, the showings made hereunder further clearly establish that catalysts formed according to the closest teaching of Wachter et al. does not yield the desired combined properties.

Example I

Fluid Cracking Catalyst According to Example 4 of U.S. Patent 6,022,471 to Wachter et al.

A catalyst product was prepared as follows:

1200 grams (silica-alumina basis) of colloid milled USY zeolite was mixed with 560 grams (Al₂O₃ basis) of colloid milled gibbsite. To this mixture was added 648 grams (SiO₂ basis) of ion-exchanged silica sol (Ludox AS-40), 800 grams (SiO₂ basis) of acid silica sol (made by reacting sodium silicate with sulfuric acid), 220 grams (Al₂O₃ basis) of an aluminum sulfate solution, as buffer, and 572 grams of kaolin clay. The resultant mixture was spray dried in a 6 ft. diameter Bowen spray dryer. The spray dried catalyst was ion-exchanged with ammonium sulfate to lower the sodium content of the spray dried product. This was followed by ion-exchange with a solution of rare earth chloride to achieve 3% RE₂O₃ on catalyst. The resultant catalyst composition had the following formulation:

30% REUSY Zeolite
20% Acid Silica Sol
16.2% Ion-Exchanged Silica Sol
14% Gibbsite
5.5% Alumina from Aluminum Sulfate
14.3% Kaolin Clay

The finished catalyst was analyzed and evaluated by conventional methods. The catalyst had a Davison Attrition Index of 7, and an average bulk density of 0.61 g/cm³. However, the catalyst had a low surface area of only 295m²/g and, after subjecting to a fluidized bed steamer under 1 atm steam for 4 hours at 1500° F (816° C), had a kinetic conversion activity of only 2.1. The full analysis is provided in Table 1 below.

Example II

Fluidized Cracking Catalyst with Maximum Zeolite Content According to Wachter et al.

Wachter et al. teach the formation of cracking catalysts having from 1 to 80 wt.% of zeolite, 5 to 50 wt.% of a gibbsite, 0.5 to 20 wt.% of a rare earth oxide and the remainder comprising a silica sol. The present sample of catalyst was produced using the maximum zeolite content taught by Wachter et al. with the remainder being composed of silica sol except for rare earth oxide near the lower limit in an attempt to provide maximum physical strength attainable.

A catalyst product was prepared as follows:

3200 grams (silica alumina basis) of colloid milled USY was mixed with 200 grams (Al₂O₃ basis) colloid milled gibbsite. To this mixture was added 600 grams (SiO₂ basis) of acid silica sol, made by reacting sodium silicate with sulfuric acid. The mixture was spray dried in a 6 ft. diameter Bowen spray dryer. The spray dried product was ion-exchanged with ammonium sulfate to reduce the sodium content in the spray dried product. The material was then ion-exchanged with a solution of rare earth chloride to achieve 0.7% RE₂O₃ on catalyst. The resultant catalyst had the following composition:

80% REUSY Zeolite
15% Acid Silica Sol
5% Gibbsite

The finished catalyst was analyzed and evaluated by conventional methods. Although the catalyst had a high surface area and, after treatment to provide a simulated equilibrium material in the same manner as described in Example I, had a kinetic conversion activity of 3.9, the catalyst was an extremely light, friable product having a Davison Attrition Index of 54 and an average bulk density of only 0.43g/cm³. Such product would not be suitable for FCC application. The full analysis is provided in Table I below.

Example III

Fluidized Cracking Catalyst According to U.S. Patent Application Serial No. 09/833,603.

A catalyst product representing the high zeolite content catalyst described and claimed in U.S. Patent Application Serial No. 09/833,603 was prepared as follows:

3750 grams (Silica-alumina basis) of preformed REUSY zeolite (according to the procedures of U.S. Patents 3,676,368 and 3,293,192) was slurried in 12,500 grams of water. 1250 grams of aluminum chlorohydrol, having a nominal formula of $\text{Al}_2(\text{OH})_5\text{Cl}$, was introduced to the slurry. The resultant mixture was colloid milled and then spray dried using a 6 ft. Bowen spray dryer. The spray dried catalyst was calcined at 750° F (400° C) for 40 minutes to remove the chlorine and set the alumina sol. The resultant dried catalyst was ion-exchanged with ammonium sulfate to lower the sodium content of the formed product. The resultant catalyst composition had the following formulation:

75 wt% REUSY Zeolite
25 wt% Alumina Sol (Aluminum chlorohydrol)

The finished product was analyzed and evaluated by conventional methods. The catalyst was a dense, strong particulate product having a low Davison Attrition Index of 12, and a high average bulk density of 0.63 g/cm³. These values show that the product can readily withstand the forces normally

encountered in a fluidized bed without being subjected to attrition to break up into fines and without being readily removed from the reaction zone. Further, the catalyst product had high surface area (602 m²/g) and pore volume (0.46 cm³/g) and, after treatment to provide a simulated equilibrium material in the same manner as described in Example I above, had a very high kinetic conversion activity of 5.0.

The formed catalytic product is highly desirable for FCC applications as it exhibits a combination of desired properties required for such application.

8. The following Table I is submitted as a summary of the analytical data obtained with respect to Examples I, II and III above.

	Example I	Example II	Example III
Analysis			
Na ₂ O, wt%	0.20	0.46	0.59
Al ₂ O ₃ , wt%	28.25	24.06	40.00
RE ₂ O ₃ , wt%	3.11	0.70	6.21
SO ₄ , wt%	0.23	0.04	2.40
Fe ₂ O ₃ , wt%	0.21	0.03	0.07
Properties			
Davison Attrition Index (DI)	7	54	12
Average Bulk Density, g/cm ³	0.61	0.43	0.63
Surface Area, m ² /g	295	673	602
H ₂ O Pore Volume, cm ³ /g	0.44	0.76	0.46
Kinetic Conversion Activity	2.1	3.9	5.0

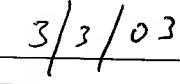
9. It is my considered opinion based on the above showing and my knowledge of the related known art that catalyst compositions composed of at least 70 wt.% of a zeolite of high activity (e.g. zeolites of Y types), when combined with an alumina sol, provide a unique catalyst useful for fluidized cracking of hydrocarbon feedstock. The present catalyst is distinct from that disclosed or suggested by Wachter et al. as well as the teachings, singly or in

combination, of the remaining references cited in the Office Action dated September 5, 2002, and noted in Paragraph 6 herein above.

Further, the present catalyst has been unexpectedly found to achieve a product capable of exhibiting high kinetic conversion activity, and provide a dense, attrition resistant product having high surface area and pore volume even though having at least 70 wt.% zeolite component therein. The resultant catalyst provides a unique combination of properties suitable for hydrocarbon fluid cracking applications, including a means for aggressively raising the activity of partially spent catalysts still in the reaction zone.

10. The undersigned declares further that all statements made herein of my own knowledge and belief are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.


Wu-Cheng Cheng


Date